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METHOD AND PROCEDURE OF SOIL ANALYSIS USED IN THE DIVISION OF SOIL CHEMISTRY AND PHYSICS

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INTRODUCTION

The method of soil analysis here outlined has been in use in the Division of Soil Chemistry and Physics of the Bureau of Chemistry and Soils since 1910. It is a product of the progressive development of soil study and represents matured judgment as to the best means by which an accurate determination of soil composition is to be obtained.

Prior to 1910 the acid-digestion method of soil analysis was in common use in the bureau. This method was supposed to show the quantities of plant food in the soil available to the plant through a long period of years.

The generally accepted belief that the acid-digestion method determined the quantity of available plant food was challenged by the results of numerous plot and pot tests. Furthermore, it was recognized that the acid-digestion method does not determine the entire composition of the soil and that results obtained by it are practically useless for studies on soil genesis. An added objection to the method has resulted from the considerable interest that has been developed in the so-called "catalytic fertilizers" and in other elements present in traces in the soil. For the determination of these trace elements at least, the acid-digestion methods are unsatisfactory. On the other hand, the method of rock analysis by

fusion with sodium carbonate was very carefully worked out by W. F. Hillebrand while chemist of the Geological Survey. These methods were first described in 1907 in a bulletin of the Geological Survey (*4*)[1] and in later revisions of the bulletin (*5*, *6*). The accuracy and thoroughness of these methods attracted worldwide attention and confidence. The chemists of the Bureau of Soils, accordingly, discarded the old acid-digestion method and adopted a fusion method closely following that of Hillebrand. Doctor Hillebrand was frequently consulted during the early development of the method adopted for soil analysis. He insisted on great purity of reagents and on double and treble precipitations when necessary; and his influence on the thoroughness and accuracy of the analyses was very important.

It is not the purpose of this bulletin to recommend this fusion method for solving soil-fertility problems, as a discussion of this phase of the problem is beyond the scope of this work.

IMPORTANCE OF THOROUGH AND ACCURATE ANALYSES

A preliminary qualitative examination is of little use in soil analysis. Soils are so complex in composition that they differ but little qualitatively. The important differences in soils are quantitative. Experience has shown that any of numerous compounds may be present in a given soil. It is obviously not practical to extend the analysis of a soil over the whole range of possible constituents. It is the practice to confine the routine analysis to the determination of the following analytical components: Organic matter, water, nitrogen, carbon dioxide present as carbonates, and the oxides of silicon, titanium, aluminum, iron, manganese, calcium, magnesium, potassium, sodium, phosphorus, and sulphur. Occasionally the presence of other elements is revealed by a low summation in the totals or by unusual behavior. Thus, copper is sometimes shown by the blue color of the solution when ammonia is added, and chromium has frequently been diagnosed by the yellow color of the sulphur fusion. In such cases the examination is extended to the determination of the indicated elements. The presence of unusual quantities of these unusual elements or the presence of extraordinary proportions of the commoner elements may have a very important influence in the crop-producing power of the soil. In any event, such unusual analyses are of great value in the study of the soil itself. Frequently, too, the soil analysis must serve many purposes, some beyond the immediate vision of the investigator. The analysis should therefore be as thorough as time and funds will permit. The quantity of elements formerly considered of little importance may be so low in soils as to limit productivity or cause physiological disturbances in the plant. Examples of these are the manganese deficiency in certain Florida marls and the magnesium deficiency in some tobacco soils. Iodine deficiencies in human food undoubtedly have their origin in soil iodine deficiencies. Included in the following discussion are procedures for some of these less common elements. For these and others fuller presentation will be found in the United States Geological Survey Bulletin 700, previously mentioned (*6*).

[1] Italic numbers in parentheses refer to Literature Cited, p. 18.

The problems of soil analysis challenge the accuracy of the most painstaking chemist. The very nature of the problem postulates dealing in traces. The phosphoric acid determination is a stumbling block to the average analyst; when phosphorus is present in traces only and in the presence of organic matter as in soils, this determination is doubly difficult. A concrete idea of the importance of accuracy in soil analysis may be had by calculating the increase of phosphoric acid and lime in the soil by adding a liberal dressing of these to the soil. An application of 200 pounds of phosphoric acid to the acre will raise the percentage of phosphoric acid in the surface soil by only about 0.01 per cent. The more liberal application of a ton of limestone per acre increases the percentage of lime by about 0.07 per cent, which represents about the limit of error of the method. Unless the reagents are very pure, and unless the utensils are very nearly insoluble, the lime from these sources will be much greater than 0.07 per cent. On the other hand, if double precipitations of the iron group are not made, the lime and magnesia found will be considerably lower than the correct value, and the alumina found will be higher.

Sulphur is occasionally a limiting factor in plant growth. The quantity of sulphur present in the soil will average even lower than that of phosphorus. Analysis of the soil for such small quantities of sulphur requires the careful application of an accurate method, or the results will be misleading.

Although the analytical operations may be performed so many times as to become mechanical, perplexing problems are continually arising. A compromise must be struck between complete washing and the solubility of the precipitate. Unusual elements and unusual proportions are of frequent occurrence. In fact, a thoroughly satisfactory soil analysis is in many ways comparable to a piece of research work.

In the following procedures, complete directions involving the fundamental processes of analytical chemistry are not given. More detailed directions may be found in Bulletin 700 of the United States Geological Survey (*6*), Hillebrand and Lundell (*7*), Mellor (*8*), and Ostwald (*9*). It is assumed that the analyst has made a few analyses of silicate ores, rocks, or cement clinker.

On the other hand, about 20 years' experience with most of the methods outlined has shown that some processes must be described in what may seem unnecessary detail. In these instances minute directions seem to be necessary for the best results.

Errors are usually caused by failure to observe exactness in the simple mechanical operations, as, for example, the failure to transfer all of the precipitates, particularly that of magnesium, the loss of soil material during ignition or fusion, and the spattering of the pyrosulphate fusion.

LIMITS OF ERROR IN SOIL ANALYSIS

The analyses of a few samples of soil taken from near-by spots in a field of apparently uniform soil show a fairly good agreement. Not enough data are available, however, to make a general statement on this question. Great variations, particularly in the phosphorus,

sulphur, and organic matter, are naturally to be expected because of the uneven distribution in the soil of residues from living organisms.

Some general statement of the allowable limits of error of analyses made by different persons on the same sample can be made from experience in this and in other laboratories. Washington (*13, p. 127*), in substantial agreement with Dittrich (*2, v. 2, p. 69*), proposes the following: For SiO_2 and other constituents which amount to 30 per cent or more of the soil mass, the limits of error may range from 0.2 to 0.3 per cent; for Al_2O_3 and other constituents which amount to from 1 to 10 per cent, the range may be from 0.05 to 0.10 per cent. As a result of the comparison of analyses of the same soil by different analysts of this laboratory somewhat larger limits for silica are recognized. It is also recognized that some determinations are subject to larger error than others of the same magnitude. For average soil composition the following limits of error have been considered satisfactory in this laboratory: SiO_2, 0.50 per cent; TiO_2, 0.05 per cent; Al_2O_3, 0.30 per cent; Fe_2O_3, 0.15 per cent; MnO, 0.003 per cent; CaO, 0.10 per cent; MgO, 0.15 per cent; K_2O, 0.05 per cent; Na_2O, 0.10 per cent; P_2O_5, 0.04 per cent; SO_3, 0.05 per cent; N, 0.005 per cent; and organic matter, 0.20 per cent. The figures are in percentage of soil and not in percentage variation. Duplicates by the same analyst should, of course, agree more closely.

In the variations mentioned it is probable that one extreme is higher than the actual figure and that the other extreme is lower. The deviation, therefore, is less than the extremes given.

The following factors contribute to the errors observed: Lack of uniformity of sample, impure reagents, contamination from glassware or other utensils, and, finally, the error incident to the method, which may be both of a personal and a chemical nature. All errors except the last may be nearly eliminated by care and by blank determinations.

As stated before, all analytical results are a compromise, usually arrived at by taking advantage of the solubility of compounds to be removed and the relative insolubility of the compound to be purified and determined. No compound is absolutely insoluble, and when relatively large quantities of easily soluble compounds must be washed from a relatively small quantity of a nearly insoluble compound an appreciable proportion of the latter may be dissolved before the former have been entirely removed. As an example, after the removal of the silica there remains an acid solution of the bases with a large excess of sodium chloride. In the precipitation of the iron group considerable ammonium chloride is added. In the precipitation of calcium as calcium oxalate, it is necessary, of course, to remove these chlorides by washing, and as the calcium oxalate is slightly soluble, some is lost and may or may not be recovered later in the analysis. The personal factor of judgment in the termination of the washing comes in at this point and will explain many discrepancies.

One reason for drawing attention to these limits of error is the practice in some quarters of stating soil analyses in terms of pounds per acre. There is a tendency to attach significance to small differences that is not warranted by the analytical figures.

Assuming that an acre of soil 6 inches deep weighs 1,750,000 pounds the limits of error for lime, potash, and phosphoric acid when calculated to pounds per acre would be as follows:

CaO (limit 0.10 per cent), 1,750 pounds per acre.
K_2O (limit 0.05 per cent), 875 pounds per acre.
P_2O_5 (limit 0.04 per cent), 700 pounds per acre.

Stated in another way, it would appear as follows: Suppose a soil on analysis gave CaO=0.30 per cent, K_2O=0.50 per cent, P_2O_5=0.08 per cent. With the above limits of error the composition might be:

	Per cent
CaO	0.35 or 0.25.
K_2O	0.525 or 0.475.
P_2O_5	0.10 or 0.06.

Or in pounds per acre:

	Pounds
CaO	6,125 or 4,375.
K_2O	9,187 or 8,312.
P_2O_5	1,750 or 1,050.

It is very plain that too much significance should not be attached to differences of a few hundred pounds of any ingredient when expressed in pounds per acre. Such variation might well be introduced because all samples are not truly representative of any considerable area of soil that may be under consideration and statements based on chemical analysis are obviously subject to some variation in sampling.

The use of standard samples of known composition and running the determinations in duplicate are the analyst's guards against error. Another important guard lies in the summation, which should not be below 99.5 per cent or above 100.75. A low summation generally means mechanical loss of silica rather than the presence of elements not stated in the analysis. Mechanical loss during the loss on ignition determination, which is common, will not, of course, be detected in the summation. The entire error in this case will be in the loss on ignition.

PREPARATION OF SAMPLE

The first and most significant part of the whole analytical operation is to secure a small, workable sample that correctly represents the composition of the particular soil. To this end, it is desirable to take large samples if the soil is nonhomogeneous, such as mottled soils, and soils in which soft concretions or masses of calcium carbonate, and ferric oxide hydrates occur. The sample may then be crushed and quartered down to a convenient size in the field.

The sample received in the laboratory is generally in the air-dried condition. If moist, it should be spread out on a sheet of clean paper and allowed to air-dry thoroughly. Clods present in the soil should be crushed with a large hardwood rolling-pin. The rolling, however, should not be vigorous enough to crush real stones. Occasionally a mass of soil material is softer than ordinary stone, yet it shows the structure of a stone. Here the operator must use his own judgment in discriminating between stone and soil.

After crushing, if crushing be necessary, the sample is thoroughly mixed, then passed through a 2-millimeter sieve. Stones and other objects not passing through the sieve are ordinarily rejected, but for special purposes it may be necessary to weigh them and determine their mineral species.

If the soil contains soft concretions of iron, lime, or manganese, it is desirable to grind roughly a large subsample before the final mixing and quartering.

The sample is well mixed and quartered down to 25 to 50 grams, depending on the number and character of the determinations to be made. It is then ground in an agate mortar and the whole sample [2] passed through a silk bolting cloth of 100 meshes to the linear inch and thoroughly mixed.

Great care should be used in sampling, grinding, and mixing. Some constituents are heavier and harder than others, and separations by gravity and by difference in toughness are likely to occur. Intelligent sampling, grinding, and mixing are absolutely essential for significant work, and if these operations must be left to laboratory helpers, it is important that the work be carefully supervised.

METHOD FOR THE MOISTURE DETERMINATION

It is not practical to oven dry the sample once for all, stopper it tightly, and weigh out subsamples when needed because the soil is hygroscopic and gathers moisture rapidly. The sample will be in an air-dry condition after sampling, grinding, and mixing. The moisture in the air-dry soil will change with the changes in moisture of the atmosphere, and it is necessary to make a moisture determination for every subsample in which major constituents are determined. Ordinarily, it is not necessary to make a moisture determination at all for constituents present in quantities of less than 1 per cent.

PROCEDURE FOR THE MOISTURE DETERMINATION

Weigh out about 2 grams of soil in a shallow weighing bottle that can be tightly stoppered. Place the weighing bottle and contents, with cover but uncovered, in a drying oven regulated at 110° C. and keep it there overnight. Cover the weighing bottle in the oven, cool in a desiccator at least one-half hour and weigh.

LOSS ON IGNITION

The loss on ignition has in some instances been taken as a measure of the organic matter. In general this is not admissible. With a very sandy soil the organic matter can be estimated by the loss on ignition, but if the soil contains considerable clay, the error is large, for the clay contains roughly 10 per cent of combined water. The loss on ignition includes the organic matter, water of combination, and any change in the state of oxidization that soil constituents may undergo. If the operation is carried out in an oxidizing flame, the error due to the last cause is negligible. The main value of the loss-

[2] This is frequently a tedious process in preparing soil samples. The sand fragments are sometimes exceedingly tough, and the toughest parts may contain unusual elements like zirconium and titanium. Not only must the operator be sure that these are ground fine enough to pass through the sieve but that these fragments are not lost by flying out of the mortar beyond the range of the paper on which the mortar rests.

on-ignition figure is to check the summation and to measure the combined water. The combined water is determined by subtracting the organic matter from the loss on ignition. The quantity of combined water is a rough estimate of the quantity of clay or colloidal matter present. Very high combined water with high alumina and occasionally with high iron oxide indicates a lateritic soil.

Although the operation for determining the loss on ignition is simple, it is not easy to obtain good duplicates, because of the difficulty of preventing slight mechanical loss and of partial reduction of the ferric oxide. The temperature at which the soil is ignited should not be too high, or ferric oxide will be changed to magnetite. Incipient fusion with incidental errors may also result. The temperature should be high enough to burn the organic matter thoroughly and to dehydrate the hydrated silicates and oxides. The temperature therefore should not be below 650° C. and not above 900°. The loss on ignition is conveniently made on the same subsample used for the major elements.

PROCEDURE FOR THE LOSS ON IGNITION

Weigh accurately from 0.5 to 1 gram [3] of soil into a 15-milliliter platinum crucible. Heat slowly in an electric furnace or over a Bunsen burner to about 700° C. and hold there one-half hour. If a Bunsen burner is used the cover should be so adjusted over the inclined crucible that the crucible contents have free access to the air. After a half hour's ignition, cool the crucible in a desiccator and weigh. Ignite an additional 15 minutes to check the constancy of weight. In this connection it should be borne in mind that ordinary platinum crucibles may lose two-tenths or three-tenths of a milligram during a half hour's ignition. Reserve the crucible and contents for the determination of the major elements.

DETERMINATION OF THE MAJOR ELEMENTS

By the major elements are meant silicon, aluminum, iron, calcium, and magnesium. Fusion with sodium carbonate is the preliminary step in the determinations. The analyst should consult Bulletin 700 of the United States Geological Survey (*6*), Mellor (*7*), and Hillebrand and Lundell (*8*) before starting the analysis.

The sodium carbonate should be the purest obtainable. In any case the blanks obtained for calcium and magnesium will be large enough to limit greatly the accuracy of the determination of small quantities of these elements.

A second evaporation is essential for the recovery of the silica, and two precipitations of the iron group are necessary to avoid the retention of considerable calcium and magnesium. Likewise two precipitations of calcium and magnesium are necessary to rid them of impurities and to secure precipitates of normal composition. Some calcium will always be found in the magnesium precipitate, and a suitable correction for this should be made.

Blanks on the reagents should be run for all the constituents determined. These blanks will be small and of little consequence for

[3] The quantity to be taken depends on the iron and aluminum content of the soil. These elements cause bulky precipitation.

the silica, iron, and alumina, but the blanks for calcium and magnesium will be considerable and very important where small quantities of these elements occur in the soil.

After the precipitation of the iron group by ammonia, it has been customary to remove manganese, nickel, copper, etc., by ammonium sulphide. This policy has been questioned. The precipitation by ammonium sulphide has the advantage that platinum, which may be in solution, is removed and will cause no further trouble. Manganese is also removed and will not contaminate the magnesium precipitate. Soils contain considerable manganese which will occasionally cause serious error if not removed. When manganese is not removed by ammonium sulphide, the magnesium precipitate will invariably contain manganese for which correction must be made, requiring the added work of a determination of manganese in the magnesium precipitate.

Evaporations should be made in platinum dishes, when possible, to avoid contamination due to solubility of glassware and porcelain. Ammoniacal solutions, especially, have a strong solvent action on glass, and if it is necessary to keep such solutions in glass for any great length of time it is better to acidify the solution. Caution must be observed against the employment of certain kinds of chemical glassware when zinc is to be determined or when zinc may influence some other determination. As much as 2 milligrams of ZnO may be dissolved from certain kinds of laboratory glassware in an ordinary analysis.

PROCEDURE FOR THE FUSION

Mix the residue from the loss-on-ignition determination with five times its weight of sodium carbonate.[4] Cover the crucible with a closely fitting cover and heat cautiously till the flux has melted and the fusion is quiet. After the fusion is quiet (or bubbling is over) apply the full heat of a good Bunsen burner or moderate heat of a blast lamp for 10 minutes longer. While the contents of the crucible are still molten, hold the crucible with the tongs and whirl or turn the crucible till the melt cools on the sides, leaving as little as possible on the botton. Cool the crucible on a slab of iron or alberene and detach the melt immediately from the cooled crucible[5] by inverting it over a 250-milliliter beaker or large platinum dish, and rolling it between the fingers with gentle pressure against the sides. Disintegrate the melt with hot water. This operation will take time. Some of the fusion will adhere to the crucible and cover and should be left covered with hot water in the receptacle chosen. After the melt is disintegrated thoroughly, wash it off the crucible and cover into the dish and add a few drops of ethanol to reduce the green manganate. Otherwise the free chlorine which is formed by the interaction of the manganate and hydrochloric acid will injure the platinum evaporating dish. If porcelain dishes are used this precaution need not be observed.

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[4] It is essential that this reagent be as pure as it is possible to obtain. It will be noted that five times as much flux as soil is used, and an impurity present in quantities of 0.1 per cent in the flux would cause an error of 0.5 per cent in the determination.

[5] If the crucible is kept well shaped by individual wooden forms and well scoured by smooth sea sand, this operation is greatly facilitated.

PROCEDURE FOR THE DETERMINATION OF SILICA

When the greenish color of the disintegrated melt has disappeared, add slowly 15 milliliters of pure concentrated hydrochloric acid to the covered receptacle. Evaporate to dryness on the steam bath. It is well to continue this heating overnight so that the separated silica gel may be sufficiently dehydrated. Take up the residue with 15 milliliters of strong hydrochloric acid and 15 milliliters of hot water, filter, and wash with hot water till practically free from chlorides. Again evaporate the filtrate to dryness in order to precipitate any silica not retained in the first precipitation, take up with 15 milliliters of concentrated acid and hot water, filter, and wash free from chlorides into a 250-milliliter beaker. Combine the two precipitates and ignite, preferably in the crucible in which the fusion was made. Ignite slowly at first to avoid mechanical loss, a common source of error in silica determinations. The light, feathery silica is easily blown by air currents. After the carbon has been thoroughly burned from the precipitate, ignite at the full temperature of the blast lamp for 20 minutes to one-half hour.[6] Check with 10-minute periods of blasting to constant weight, bearing in mind that the crucible itself may lose one-tenth or two-tenths of a milligram during this time. When the weight has become constant, moisten the silica with water, add 6 to 8 milliliters of strong hydrofluoric acid and a few drops of sulphuric acid, and evaporate cautiously to dryness. If the residue is more than 3 or 4 milligrams, treat again with a few milliliters of hydrofluoric acid. Ignite the crucible for a minute or so over a blast lamp, cool, and weigh. The loss in weight represents the silica. Save the crucible and contents for the ignition of the iron group.

PROCEDURE FOR THE DETERMINATION OF IRON OXIDE, ALUMINA, AND TITANIA

The filtrate from the silica determination containing the iron and aluminum, titanium, and other elements is now in a 250-milliliter beaker. Neutralize this filtrate with a solution of pure ammonia,[7] using the precipitate as an indicator. Make only very slightly acid with hydrochloric acid and heat to boiling. Precipitate the group with a slight excess of dilute ammonia. An excess of 2 to 3 milliliters of strong ammonia diluted with its own volume of water is sufficient. Boil a minute or so and filter into a 400-milliliter beaker when hot, allowing the precipitate to settle first. An 11-centimeter filter paper will ordinarily be required to hold the precipitate from the average soil. Wash only slightly, as this is but the first precipitation. Transfer the filter paper with its contents to the beaker in which the precipitation was made and dissolve in 10 milliliters of strong hydrochloric acid and hot water, macerate the filter paper[8]

[6] This blasting is necessary to obtain constant weight. No matter how careful the washing has been, some sodium chloride (1 to 3 milligrams) will be given off in the first stages of the blasting. See Hillebrand and Lundell (7, *p.* 545).

[7] This ammonia should not contain an appreciable quantity of carbonate or other dissolved material. The ammonia that comes from the manufacturer is generally satisfactory, but if it must be kept for a long time it is best kept in parafined bottles.

[8] The presence of this macerated filter paper is important to facilitate the second washing of the iron group and the dissolving of the ignited precipitate in potassium pyrosulphate.

with two glass rods and add enough water to make the volume up to 150 milliliters, precipitate the iron group as before, filter, and wash thoroughly with hot water, containing about 1 per cent ammonium nitrate in later washings, till the wash water is practically free from chlorides.

Without removing the precipitate from the filter paper, transfer it to the crucible used for the silica determination, dry and ignite in an inclined crucible with the cover so adjusted as to allow the free access of air. Ignite over a blast for 15 minutes, or to constant weight.

DISSOLVING THE IRON GROUP PRECIPITATE

Transfer the bulk of the ignited iron group precipitate to a capacious platinum crucible (30 to 40 milliliters), add 5 to 7 grams of potassium pyrosulphate, and heat very cautiously [9] over a low-flame Bunsen burner, keeping the crucible covered. A small quantity of the potassium pyrosulphate is fused in the smaller crucible in which the iron group was ignited until the contents not transferred to the larger crucible are dissolved. Fuse the contents of the crucible till all the solid matter has dissolved (*6, p. 117*). If any undissolved matter adheres to the sides of the crucible after the boiling has receded, bring it into the melt again by manipulation with the tongs and flame. After fusion is complete, cool the melt as in the sodium carbonate fusion, add 4 milliliters of strong sulphuric acid and dissolve in water, taking care to keep the volume under 150 milliliters.

REDUCTION AND TITRATION OF THE IRON

Pass hydrogen sulphide into the solution of the iron group just obtained to precipitate the dissolved platinum and to reduce the iron. Boil a few minutes to coagulate the sulphur and filter into a 300-milliliter iron reduction flask. Make the volume up to about 200 milliliters and pass hydrogen sulphide through the cold solution at first, then bring slowly to a boil while the hydrogen sulphide is still passing. Cool about 10 minutes (the hydrogen sulphide still bubbling through). Then disconnect the hydrogen sulphide tube and boil off the hydrogen sulphide by passing through a current of carbon dioxide. Test for complete expulsion of hydrogen sulphide by means of a piece of filter paper moistened with lead acetate and held at the opening of the tube. When the sulphide is completely expelled, cool without interrupting the carbon dioxide stream and titrate with standard permanganate. If unfamiliar with the process, reduce again and check the titration.

PROCEDURE FOR THE DETERMINATION OF TITANIUM

Evaporate the liquid from the iron titration to 50 to 75 milliliters, add 10 milliliters of concentrated sulphuric acid and a few drops of hydrogen peroxide,[10] make up to 100 milliliters and compare the color with a standard titanium solution treated in the same manner.

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[9] This fusion is likely to froth and boil over, and in addition there is considerable mechanical loss by spattering unless the operation is carefully performed.

[10] The hydrogen peroxide should be free from hydrofluoric acid.

PRECIPITATING THE AMMONIUM SULPHIDE GROUP

Evaporate the combined filtrates from the iron group, preferably in a platinum dish, to slightly less than 100 milliliters, transfer to a wide-mouthed Erlenmeyer or assay flask, add 2 to 3 milliliters of strong ammonia, pass in hydrogen sulphide to saturation, add 2 to 3 milliliters of strong ammonia, and then stopper and let stand overnight. Manganese, copper, and zinc are precipitated. Filter and wash with ammonia and ammonium sulphide solution.

PROCEDURE FOR THE DETERMINATION OF CALCIUM

To the hot filtrate from the ammonium sulphide precipitation which should not exceed 150 milliliters in volume, add an excess of recently dissolved ammonium oxalate and digest several hours on the steam bath. Cool and filter through the finest filter paper. Ignite the precipitate to render the coprecipitated platinum insoluble, dissolve in dilute hydrochloric acid, reprecipitate as oxalate, filter, ignite, blast, and weigh. Add the filtrate from the second precipitation to that of the first, as it may contain magnesium.

PROCEDURE FOR THE DETERMINATION OF MAGNESIUM

The combined filtrates from the calcium determination should not exceed 175 milliliters. If necessary evaporate to this volume. To the cool filtrates add an excess of any soluble orthophosphate slowly and with constant stirring; add enough strong ammonia to make the solution about 5 per cent NH_4OH and let stand overnight in a cool place. Filter and wash with 2.5 per cent NH_4OH. Dissolve the precipitate in dilute hydrochloric acid, add only a slight excess of the orthophosphate solution (not more than 2 milliliters of a 10 per cent solution), and slowly add ammonia with constant stirring till the precipitate commences to form. Add enough strong ammonia to make the solution about 5 per cent NH_4OH. Let stand about two hours or longer and filter and wash with 2.5 per cent NH_4OH till free from chlorides. Dry the precipitate and ignite slowly. The full heat of a good Bunsen burner will ordinarily serve to burn the precipitate white, but occasionally a weak blast is necessary. It is a mistake to blast the precipitate till it fuses to the wall of the crucible.

Calcium is always present in the magnesium precipitate. The quantity present should be determined and suitable corrections applied. To accomplish this, dissolve the magnesium pyrophosphate in a small quantity of dilute sulphuric acid. Add enough absolute alcohol to make the solution 90 per cent alcohol and allow to stand three or four hours. Filter and wash with alcohol. Dissolve the precipitated calcium sulphate in hot acidulated water, precipitate the calcium as oxalate, ignite, and weigh. It is the general experience that, if the procedure is uniform in all cases, the quantity of calcium found in the magnesium precipitate will be so uniform that an average correction can be applied in later analyses without making the actual separations. If no calcium oxalate precipitate is obtained in the calcium determination, there is probably not enough calcium present to saturate the solution, and in such cases the quantity of calcium that may be present must be separated from

the magnesia precipitate. Manganese should not contaminate the magnesia precipitate if the precipitation by ammonium sulphide has been carefully done. If the ammonium sulphide precipitation has not been used, a separate determination for manganese in the magnesia precipitate must be made and suitable corrections applied.

PROCEDURE FOR THE DETERMINATION OF POTASSIUM AND SODIUM

Here a warning on the purity of reagents must be repeated. The well-known J. Lawrence Smith method is used, and in this method eight times as much flux as soil is used. The calcium carbonate used should contain not more than 0.02 per cent combined potash and soda, and a reagent of such purity is not easily obtained.

For the determination, weigh out 0.5 gram of the soil and mix intimately with 0.5 gram ammonium chloride and 4 grams calcium carbonate [11] in an agate mortar, transfer the sample to a J. Lawrence Smith crucible, rinsing out the mortar with a small quantity of calcium carbonate. Place the covered crucible through a hole in the side of a baked clay or alundum cylinder in such a position that the covered end extends about one-half inch beyond the outside wall. Turning the crucible in the earlier stages of ignition will facilitate the detaching of the sintered cake. Ignite slowly at first till the crucible ceases to smell of ammonia, then apply the full heat of one or two Bunsen burners to the lower end of the crucible for about three-quarters of an hour.

Slake the sintered cake in a little water, wash out the crucible and cover, and leach on the filter till the wash water reaches about 150 to 200 milliliters. Precipitate the calcium as carbonate with ammonium carbonate and ammonia. Filter, wash the calcium carbonate one or two times by decantation, then dissolve it in a minimum quantity of hydrochloric acid, and reprecipitate as before. Evaporate the combined filtrates in a platinum dish and drive off the ammonium salts at a temperature not to exceed 525° C.[12]

Take up the residue in hot water, precipitate the small quantity of calcium that may be present with a few drops of ammonium oxalate, and filter into a platinum dish. Evaporate to dryness and ignite to expel ammonium salts as before. When the residue has burned white, moisten with a few drops of dilute hydrochloric acid, evaporate, ignite as before for a few minutes, cool, and weigh. Take up in water, filter through a small filter into a porcelain or glass evaporating dish, and wash. Place the filter paper in the small platinum dish, ignite, and weigh. Subtract the weight so obtained from the weight of the dish plus the double chlorides. This gives the weight of the sodium and potassium chlorides. Determine the potassium by precipitation with enough platinic chloride to react with the quantity of chlorides weighed up. Evaporate to pastiness, take up with 80 per cent ethanol, collect on a Gooch crucible, dry at 110° C., and weigh. Run blank tests on the reagents used, including evaporation, like the regular determinations if the evaporations are not made in platinum. Failure to run blanks and apply suitable corrections is not admissible in the determination of potash and soda.

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[11] A small quantity of calcium carbonate put into the bottom of the crucible will facilitate removal of the sintered cake.

[12] This is best done in an automatically regulated electric furnace.

PROCEDURE FOR THE DETERMINATION OF MANGANESE

It is convenient to combine the manganese and phosphorus determination. Weigh out 2 grams of soil into a platinum dish, add a few milliliters of nitric acid, the quantity depending on the quantity of organic matter present, evaporate, and ignite at the full heat of a Bunsen burner for about one-half hour. Treat the ignited residue with 20 milliliters of strong hydrofluoric acid and from 5 to 10 milliliters of nitric acid overnight. Evaporate on the steam bath to dryness. Add nitric acid, evaporate to dryness as before, and repeat this addition of nitric acid and evaporation to dryness twice, in order to free the material from fluorides. (If manganese only is to be determined it is advisable to use sulphuric acid instead of nitric acid. In this case fluorides are more easily decomposed by heating the sulphuric acid to fuming, adding water, and repeating the evaporation and fuming.) Take up with water, add a few drops of sulphurous acid to dissolve any manganese dioxide that may have been formed, then add 5 milliliters of nitric acid, and filter into a 100-milliliter measuring flask. When cool, make up to volume and withdraw 25 milliliters for the manganese determination and reserve the remaining solution for the phosphorus determination. Place the 25 milliliters in a 50 or 100 milliliter measuring flask, add 0.004 gram of silver nitrate for every milligram of metallic manganese estimated to be present. (Ordinarily it is safe to add 0.008 gram of silver nitrate.) Add 5 milliliters of nitric acid for each 100 milliliters of flask capacity and 1 gram of ammonium persulphate, then heat on the steam bath till the color is developed. If a brownish precipitate forms at this stage and does not dissolve on heating for 10 or 15 minutes, too little silver nitrate has been added. In that case reduce with a few drops of sulphurous acid, add more silver nitrate, and develop the color again. Compare in a short tube colorimeter with a standard manganese solution treated as above. The manganese solution is conveniently made by reducing a permanganate solution of known strength. It is permissible to report the results for manganese to three significant figures beyond the decimal. The determination is accurate, and small quantities are significant. If desired, one may also use the periodate as described by Hillebrand and Lundell (*7, p. 350*).

PROCEDURE FOR THE DETERMINATION OF PHOSPHORUS

To the solution obtained under the manganese procedure, add enough ammonia to partly precipitate the iron, clear with a few drops of nitric acid, and add enough nitric acid to make the solution about 4 per cent with respect to this acid. Heat to 60° C. and add 10 milliliters of 10 per cent ammonium molybdate,[13] stir vigorously (preferably with a mechanical stirrer or shaker), cool, and let stand two hours or more, then filter and wash with water acidulated with nitric acid. Punch a small hole in the bottom of the filter paper and wash the phosphomolybdate with dilute ammonia into the beaker in which the precipitation was made. The precipitate should completely dissolve, with the exception of a negligible quantity, gen-

[13] Best made by dissolving pure molybdic acid in the requisite quantity of ammonia. This solution is used on account of its permanence, and ease in regulating the nitric-acid content of the solution in which precipitation is made.

erally not more than one-tenth or two-tenths of a milligram. If, because of abnormal composition of the soil or faulty manipulation, the precipitate appears to exceed that amount, put in a small crystal or so of citric acid. If this fails to dissolve the precipitate, filter, fuse the precipitate with a bit of sodium carbonate, then extract and precipitate the phosphorus as above.

To the ammoniacal solution of the phosphomolybdate add nearly, but not quite, enough hydrochloric acid to cause the formation of the yellow precipitate, then add 5 milliliters of magnesia mixture, slowly and with constant stirring. Add ammonia drop by drop, stirring continually, and, after the precipitate has formed, add enough strong ammonia to make the solution 5 per cent NH_4OH. Let stand at least two hours in the cold, then filter and wash with 2.5 per cent ammonia. The precipitated ammonium-magnesium phosphate adheres tenaciously to the beaker, and precautions should be taken for its quantitative removal. The same procedure is to be followed in igniting this precipitate as in the ignition of the magnesia precipitate.

PROCEDURE FOR THE DETERMINATION OF SULPHUR

Fuse from 1 to 2 grams of soil (or twice this quantity if chlorine is also to be determined) in a 15-milliliter platinum crucible with five times the weight of sodium carbonate and two-tenths or three-tenths of a gram of sodium nitrate. This fusion is best made in an electric furnace. If gas is used for the ignition, provide a shield for the crucible as described by Hillebrand to avoid sulphur contamination. After fusion, the melt is thoroughly disintegrated with water on the steam bath, preferably overnight. It is then filtered (into a measuring flask if chlorine is to be determined) and made up to 150 to 175 milliliters if it is not already of this volume. Add enough hydrochloric acid in excess of the quantity calculated to neutralize the sodium carbonate to make the solution about 1 per cent HCl. Bring to a boil and precipitate the sulphates with 10 milliliters of 10 per cent barium chloride, cool, filter onto a small fine filter, and wash. Ignite at a low temperature and weigh. Occasionally, due to long digestion or too large an excess of acid, the silica will gel. The following two procedures may then be followed: The silica may be removed by evaporation and filtration, or it may be removed by precipitating the neutralized solution with ammonia. The ignited barium sulphate should be treated with a drop of hydrofluoric and sulphuric acids, cautiously ignited, and weighed again to avoid possible contamination by silica. The reagents used invariably contain some sulphur, and blanks should always be run alongside and treated in the same manner as the determinations.

PROCEDURE FOR THE DETERMINATION OF CHLORINE

Acidify an aliquot of the solution of the sodium carbonate fusion equivalent to 2 grams of soil with the calculated quantity of nitric acid. Make the solution about 1 per cent with nitric acid and precipitate the chlorine with silver nitrate. If the fusion is taken up with a comparatively large quantity of water and digested on the steam bath before filtration there will be no difficulty with the separation of silica. The volume of the solution should be from 150

to 200 milliliters for 2 grams of soil. If there is evidence that the silica is separating out or if the analyst has had previous difficulty with the separation of silica, the silica may be removed by adding ammonia to the neutralized solution and boiling momentarily and filtering, or the solution may be evaporated to dryness after acidifying.

PROCEDURE FOR THE DETERMINATION OF FLUORINE

Merwin's method (*6, p. 228*) depending on the bleaching of pertitanic acid by fluorine has been applied to soils by Steinkoenig (*12*).

Fuse 2 grams of the rock powder with 6 grams of mixed sodium and potassium carbonate. Disintegrate the mass with 250 milliliters of water. Add a solution of 3 grams of ammonium carbonate to the mixture and filter. Add 1 gram of ammonium carbonate to the filtrate and evaporate slowly to 50 milliliters and filter into a 100-milliliter measuring flask. A standard solution of titanium sulphate containing 0.01 gram of TiO_2 and a few drops of strong hydrogen peroxide are added, and the solution is neutralized by dilute H_2SO_4 (1 to 3), as indicated by the appearance of an orange color. Three milliliters of concentrated sulphuric acid are added, the solution is cooled and made up to volume. The solution is compared to a standard of the same concentration and acidity. The difference between the test reading with the standard set at 100 in the colorimeter divided by 23,000 gives the grams of fluorine in the sample.

PROCEDURE FOR THE DETERMINATION OF NITROGEN

The Gunning-Hibbard method is followed (*1, p. 27*).

Digest from 1 to 10 grams of soil (depending on the nitrogen content) in a 500-milliliter Kjeldahl flask with 30 to 40 milliliters concentrated sulphuric acid and approximately 10 grams of a salt mixture composed of 10 parts potassium sulphate, 1 part ferrous sulphate, and one-half part copper sulphate. Continue the digestion till the mixture is colorless or nearly so. After cooling, dilute the contents of the flask with water, add an excess of approximately 45 per cent sodium hydroxide solution, connect with a condenser and distill 150 milliliters into standard acid. The distillation may be carried out in a digestion flask, or, if preferred, the solution may be transferred to a copper flask. Titrate the excess of acid with 0.1 N alkali, using methyl orange or cochineal as an indicator.

PROCEDURE FOR THE DETERMINATION OF ORGANIC MATTER

It is inadmissible to use the loss-on-ignition figure for organic matter except as the roughest approximation for highly organic or very sandy soils. Two methods may be used, the combustion method and the hydrogen-peroxide method. The combustion method makes use of an empirical factor for converting the carbon dioxide to organic matter. This empirical factor seems to be approximately correct for the average soil, but may be in error as much as 75 per cent for certain soils.

The combustion is conveniently made in a multiple-unit electric furnace and a quartz tube.

Fill the portion of the quartz tube lying within the last long unit loosely with finely divided asbestos[14] and heat the furnace to about 900° C., meanwhile passing a stream of oxygen slowly through the tube. After the tube and asbestos have become thoroughly decarbonized, attach a drying absorption bulb of strong sulphuric acid, then a small absorption tube of phosphoric acid and finally a good Fleming bulb containing soda lime and phosphoric acid. Use another filled Fleming bulb as a tare when weighing and turn the inlets of both bulbs open to the air for a moment or so shortly before weighing. This is important to adjust differences in atmospheric pressure. Run a current of oxygen slowly through the apparatus for one-half hour and weigh the absorption bulb. Repeat the operation and make such adjustments as are necessary to obtain constant weight. When the bulb has attained constant weight, and the asbestos end is still at about 900° C., introduce from 0.1 to 5 grams of the soil (depending on the organic content) in a porcelain or platinum boat into the tube in the middle section of the furnace. Heat the first and middle sections till the temperature reaches about 900°, meanwhile passing a steady stream of oxygen. After the contents of the combustion boat have reached 900°, pass enough oxygen to sweep out the combustion tube about four to six times, remove and weigh the bulb. An additional 15-minute run should be made to see that the bulb has reached constant weight. Multiply the weight of carbon dioxide obtained by 0.471[15] to reduce to organic matter. If carbonates are present, the carbon dioxide from this source must be deducted.

The hydrogen peroxide method has been described in detail in a previous article (*11*). This method has the advantages of determining the organic matter directly, without the use of an empirical factor, and the coal, graphite, and charcoal, which get a double count in the combustion method, are largely eliminated. Its disadvantages are that it is not directly applicable to soils containing more than 1 per cent of calcium carbonate or more than very small quantities of manganese dioxide, and the manipulations necessary to insure good contact of the floating organic matter with the decomposing liquid, and to secure clear filtrates are not always easy. There are carbonaceous substances in addition to charcoal and graphite that are not decomposed by hydrogen peroxide. These include paraffin-like substances. It is a debatable question whether or not these substances should be considered soil organic matter.

To determine the organic matter by the peroxide method, weigh accurately about 1 gram of soil or 0.2 gram of peat or muck into a tall 150-milliliter beaker. Add 10 milliliters of water and 10 milliliters of 30 per cent hydrogen peroxide. Cover the beaker and watch a few minutes. In the absence of a vigorous reaction[16] place the beaker on a steam bath and digest till no more bubbles are evolved. Manipulate the beaker, with a stirring rod if necessary,

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[14] The additional heat obtainable in the quartz tube renders the use of cupric oxide or other catalysts unnecessary. Cupric oxide invariably shortens the life of the quartz tube.

[15] This factor, known as the Van Bemmelen factor, represents quite satisfactorily the mean ratio of carbon dioxide to organic matter, but it must be recognized that in individual cases the range of error is wide and the actual percentages of organic matter are at best only good approximations.

[16] A vigorous reaction with the evolution of heat shows the presence of manganese dioxide. If the quantity of manganese dioxide is small (for instance, less than 0.25 per cent) it can be destroyed by evaporating with a very small excess of oxalic acid. If much manganese dioxide is present, the method is not applicable.

in order to bring the lighter particles of organic matter in contact with the solution. When the reaction is complete, wash the residual matter onto a thick and compact asbestos pad in a glass Gooch crucible fitted with an accurately ground-on cover. Wash with enough water to carry through the soluble matter. Evaporate the filtrate in a tared platinum dish, ignite, and weigh the residue.

Dry the soil in the Gooch crucible for 18 hours at 110° C, and weigh. Run a moisture determination on the original sample at the same time. The difference in weight between the moisture-free material and the dried residue plus the ash obtained from the solution is the weight of the organic matter. The filtrate from the peroxide digestion should be practically clear. Occasionally heavy clay soils will give a turbid or muddy filtrate. If running this through the pad a second time fails to remove the suspended matter, certain corrections must be made. Make up the turbid filtrate to a definite volume. After mixing and settling, evaporate the clear upper half, ignite, and weigh. The weight of the residue from the lower half less the residue from the upper half gives the weight of ignited clay. Increase this by one-ninth to give the weight of the clay at 110° and add this to the weight of the residue in the Gooch crucible.

PROCEDURE FOR THE DETERMINATION OF COMBINED WATER

The quantity of combined water is roughly a measure of the clay present in the soil. The determination is of considerable importance in clays or soil colloids. The combined water is obtained by subtracting the organic matter from the loss on ignition. When the organic matter is determined by the combustion method, the combined water may be in error owing to the use of an average factor for organic matter. It is believed that a more nearly accurate figure for the combined water may be obtained by determining the organic matter by hydrogen peroxide, then determining the carbon in the residue from the hydrogen peroxide determination by combustion, assuming that this carbon forms 90 per cent of the combustible matter present in the residue.

PROCEDURE FOR THE DETERMINATION OF CARBON DIOXIDE FROM CARBONATES

Carbonates are restricted to soils of certain regions, and even there they may be present in certain horizons only. However, it is best to test for carbonates all samples received for analysis. To do this place about 10 grams of soil in a small beaker, cover with water, and let stand till thoroughly moistened. Add about 20 milliliters of dilute hydrochloric acid [17] (1 to 1), stir, and note any effervescence that may occur. In the absence of effervescence it is not certain that some carbonates are not present, and the beaker and contents should be heated just short of boiling. Effervescence under these conditions shows the presence of dolomite.

To determine the carbonates quantitatively, weigh 0.5 to 10 grams of soil into the decomposition flask of a Knorr apparatus. Add

[17] This procedure will have to be revised, as E. C. Shorey, of the Bureau of Chemistry and Soils, has found that the organic matter of many soils contains uronic acid which splits off carbon dioxide when boiled with hydrochloric acid of this strength.

dilute hydrochloric acid (1 to 2) in considerable excess and boil till decomposition and absorption are complete. Use a solution of silver sulphate in the absorption train to take out any traces of hydrochloric acid that may come over. Precautions should be taken to dry the gases over the same reagent just before entering, and in the carbon dioxide absorption bulb. For this purpose phosphoric acid has given the best result.

PROCEDURE FOR THE DETERMINATION OF OTHER ELEMENTS

It is occasionally necessary to determine other elements in soils. Considerable experience has shown that the methods given by Hillebrand for the determination of barium, zirconium, chromium, vanadium, rare earths, zinc, and copper are satisfactory when applied to soils. Hillebrand's (*6*) scheme for determination of nickel, cobalt, and strontium have not been so satisfactory, though the method given for strontium is probably the best to be had. Small quantities of nickel are easily determined by the dimethylglyoxime method (*7*, *p. 315.*) However, this method is not directly applicable to soils as the nickel must first be separated from the excessive quantities of iron and aluminum that are present in normal soils.

For lithium, rubidium, and caesium, a method given by Gooch and Phinney (*3*, *p. 392*) and modified by Robinson (*10*, *p. 50–51*) has given satisfactory results.

For the analysis of soils for elements not covered in the above scheme the analyst should consult Hillebrand and Lundell (*7*).

SUMMARY

The fusion method of soil analysis developed for use in the soil chemistry laboratory of the Bureau of Chemistry and Soils is described. Directions are given for the preparation of the soil sample after it reaches the laboratory. The limits of error allowable in a satisfactory analysis are discussed, and the limits of error for various elements are given in percentages and in pounds per acre.

Methods and procedures are given for the determinations of moisture, loss on ignition, organic matter, chlorine, fluorine, and the oxides of silicon, titanium, aluminum, iron, manganese, calcium, magnesium, potassium, sodium, phosphorus, and sulphur.

The method is designed to show accurately the ultimate composition of the soil for scientific purposes and has only a very general application to problems involved in soil-fertility studies.

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